



Cross-linked high conductive membranes based on water soluble ionomer for high performance proton exchange membrane fuel cells



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HIGHLIGHTS

- Prepared the water soluble polymer as an ionomer in the catalyst layer of DMFCs.
- “Click” reaction was selected in order to make the membranes.
- The cross-linked membranes possess high proton conductivity.

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ABSTRACT

In this paper, a series of proton exchange membranes prepared by “Click Reaction” are reported. The cross-linked membranes are based on water soluble sulfonated poly (ether ether ketone) containing dipropenyl groups (SDPEEK-nE/nH). Compared with self-crosslinked membranes (SDPEEK-nS), this “Click” cross-linked membranes using 1,2-Ethanedithiol and 1,6-Hexanedithiol as the cross-linker exhibit extremely reduced water uptake and swelling ratio. The lowest proton conductivity at 80 °C of the “Click” cross-linked membranes reaches to 0.168 S cm⁻¹, and the highest methanol permeability of the “Click” cross-linked SDPEEK-8E is only 4.13 × 10⁻⁷ cm² s⁻¹, which is 5 times lower than that of Nafion 117 membrane. All the results imply that the cross-linked membranes with novel thiol cross-linker are promising alternative material for fuel cell application.

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1. Introduction

Direct methanol fuel cells (DMFCs) are capable of converting chemical energy from methanol directly into electricity, providing clean and efficient energy sources for stationary, traction, and portable applications [1]. As one of the core components of DMFCs, proton exchange membranes (PEMs) have supplied ionic pathways for proton-transfer as well as acted as a separator between the anode and the cathode [2–4]. Nafion, a commercially available PEM, shows excellent chemical resistance, high proton conductivity and mechanical stability at moderate temperature (<90 °C). Meanwhile, Nafion possesses high solubility in low-boiling-point solvents such as methanol and water as an ionomer for use in the

catalyst layer to build an efficient three-phase boundary [5]. However, due to the high cost and high methanol permeability of Nafion, researchers need to investigate a promising material as a substitute for Nafion [6–8].

Up to now, many kinds of alternative materials have been developed such as sulfonated aromatic polymers [9–11], poly-benzimidazoles [12,13], polyimides [14] and polyphosphazene [15]. Among them, sulfonated poly(ether ether ketone)s (SPEEKs) have aroused great interest due to their high proton conductivity, excellent mechanical properties and acceptable cost of production [16]. What's more vital is that if the SPEEKs have a highly degree of sulfonation, they will possess high solubility in low-boiling-point solvents the like Nafion. However, high degree of sulfonation introduces a series of problems, such as extremely high water uptake and methanol permeability, large dimensional variations and inadequate mechanical properties that render the membranes

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unsuitable for DMFCs [17–21]. Therefore, we hope to synthesize a series of SPEEKs not only have enough properties to be used for PEMs, but also can be used as an ionomer for use in the catalyst layer of DMFC.

Crosslinking is regarded as an effective method to overcome these deficiencies, which can not only suppress excess water uptake, methanol permeability and swelling ratio but also improve the mechanical and chemical stabilities [22–24]. There were several studies about the cross-linking of sulfonated polymers. For example, Phu and his co-workers reported a cross-linked membrane, which used 4, 4'-oxybis(benzoic acid) as the cross-linker displaying high water uptake because of the low cross-linked density of the membranes [25]. Recently, Lee et al. prepared a cross-linked membrane, which used 4-(trifluorovinyl)-biphenyl-2,5-diol (TFVOH) as the cross-linkable moiety, displayed excellently low water uptake and swelling ratio because of the high cross-linked density of the membranes [26]. The selection of the cross-linker is crucial to the preparation of membranes with good performance.

"Click" Chemistry has gained a lot of attention from many scientists for their high selectivity, efficiency and moderate operating condition [27]. It has been introduced by Sharpless to create new polymer architectures such as block copolymers, star-shaped polymers, cyclic and dendritic macromolecules [28]. As one important field of "Click" Chemistry, thiol-ene (TE) reactions have been deeply studied due to the wide application of commercially available thiols and alkenes [29]. For example, Hawker demonstrated the use of TE "Click" reactions for the formation of mono-disperse dendrimers [30]. And Schlaad successfully utilized this method to the functionalization of 1,2-polybutadiene side groups [31]. Therefore, we have been enlightened how to construct novel three-dimensional networks without traditional cross-linker between the chains of the polymer.

In our previous work [32], we have prepared a series of water soluble polymers (SDPEEK-7/SDPEEK-8) as the matrixes. For the "Click" reaction, we selected different cross-linker (1,2-Ethanedithiol and 1,6-Hexanedithiol) for creating the cross-linked membranes under moderate conditions. The results showed that, those two kinds of crosslinked membranes were more suitable than the membranes which cross-linked with BPO for PEMs, meanwhile the matrix polymer could be used as an ionomer in the catalyst layer of DMFCs.

2. Experimental section

2.1. Materials

2,2-Diallyl bisphenol A was supplied by Hubei Research Institute of Chemistry. 4,4'-Difluorobenzophenone (DFB) was supplied by the Longjing Chemical plant. 5,5'-Carbonyl-bis(2-fluorobenzenesulfonate) (SDFB) was synthesized according to the literature [33] and was recrystallized before use. 1,2-Ethanedithiol (98%) and 1,6-Hexanedithiol (97%) were purchased from Aladdin Chemistry Co., Ltd., China. Benzoyl peroxide (BPO) was provided by Sinopharm Chemical Reagent Co., Ltd., China. N-Methyl-2-pyrrolidone (NMP) and Dimethyl sulfoxide (DMSO) were vacuum-distilled and were stored over 4 Å molecular sieves. All other solvents were obtained commercially and used without further purification.

2.2. Synthesis of SDPEEK-7/8

The synthesis of original polymer was illustrated by preparation of SDPEEK-8. Diallyl bisphenol A (6.16 g, 0.02 mol), DFB (0.872 g, 0.004 mol), SDFB (6.752 g, 0.016 mol) were added to a three-neck bottom flask equipped with a mechanical stirrer, a nitrogen inlet

and a Dean–Stark trap. DMSO/toluene (45 ml/20 ml) was used as a solvent in this reaction. The resultant mixture was stirred for 3 h at 140 °C under nitrogen atmosphere to remove water by azeotropic distillation. Then slowly raised the temperature to 180 °C and maintained at that temperature for 16 h. After being washed with cool deionized water for several times, the polymer was isolated by filtration and dried at 70 °C in vacuum for 3 days to obtain the product. Table 1 shows the water solubility of the matrix polymer powder.

¹H NMR (500 MHz, DMSO-*d*₆, δ , ppm): 6.33 (HC=C of propenyl groups *ortho* to methyl), 6.66 (HC=C of propenyl groups *ortho* to aromatic group), 8.2 (ArH *ortho* to –SO₃Na groups), 6.8–7.8 (other ArH).

2.3. Preparation of the cross-linked membranes

The cross-linked membranes were prepared by solution casting method. Firstly, 1 g of SDPEEK sample in sodium form was dissolved in NMP at room temperature to prepare a 10 wt% solution. A certain content of three different types of cross-linking agents (BPO 0.5 g, 1,2-Ethanedithiol 1 ml, 1,6-Hexanedithiol 1 ml) was then added to the solution, respectively. The resulted solution was cast onto a glass plate around with the eaves and sealed with another glass plate, then heated at 60 °C for 16 h. The membranes were then peeled off from the substrates. Then the membranes were dried under vacuum at 80 °C for 4 h to and then immersed into a 1 M HCl solution for 48 h. The membranes were washed with the deionized water for several times to get acid form membranes. The membranes were described as SDPEEK-nS, SDPEEK-nE, SDPEEK-nH on the basis of different types of cross-linking agents, BPO, 1,2-Ethanedithiol, 1,6-Hexanedithiol, respectively.

2.4. Characterization

2.4.1. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) measurements were performed on a Perkin–Elmer TGA-2 thermogravimetric analyzer from 80 to 700 °C at a heating rate of 10 °C min^{−1} under N₂ atmosphere. Before the heating scan, all the samples were pre-dried under N₂ at 120 °C for 10 min to remove the residual water and solvent.

2.4.2. Mechanical properties

The mechanical properties of the thin dry membranes were evaluated at room temperature on SHIMADZU AG-I 1KN at a speed of 2 mm min^{−1}. The size of the samples was 15 mm × 4 mm. Before testing, all the membranes were dried in the oven at 80 °C for 4 h.

2.4.3. Ion exchange capacity (IEC)

The IEC of the membranes was determined by a classical titration method. The membranes in acid form were marinated in 1 M NaCl solutions for 24 h to exchange the H⁺ ions to Na⁺ ions completely. The H⁺ ions in solution were then titrated with 0.01 M NaOH using a phenolphthalein indicator.

Table 1
Water solubility of SDPEEK-7/8 powder.

Polymer powder	Temperature of water (°C)				
	0	20	40	60	80
SDPEEK-7	Sw ^a	Sw	S	S	S
SDPEEK-8	Sw	S	S	S	S

^a Sw, swollen; S, soluble.

The ion-exchange capacities were calculated from:

$$\text{IEC} = \frac{\text{consumed NaOH} \times \text{molarity NaOH}}{\text{weight of dried membrane}} (\text{mequiv g}^{-1}) \quad (1)$$

2.4.4. Water uptake and swelling ratio

The water uptake and water swelling ratio of the membranes were determined by measuring the change in the weight and thickness between the dry and swollen membranes. First, the membranes were dried at 80 °C under vacuum for 12 h until constant weight were obtained. Then the membranes were taken out which had been immersed into deionized water at the desired temperature for 24 h. Wiped with tissue paper, and measured their weight and thickness as soon as possible. Water uptake (WU) of the membranes was calculated from:

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

where W_{dry} and W_{wet} are the weight of dry and corresponding water-swollen membranes, respectively.

The swelling ratio was calculated by the following equation:

$$\text{Swelling ratio (\%)} = \frac{T_{\text{wet}} - T_{\text{dry}}}{T_{\text{dry}}} \times 100\% \quad (3)$$

where T_{dry} and T_{wet} are the thickness of dry and corresponding water-swollen membranes, respectively.

2.4.5. Proton conductivity and methanol permeability

The conductivity of the cross-linked membrane was measured using a modified four-probe AC impedance method from 0.1 Hz to 100 kHz, 10 mV AC perturbation and 0.0 V DC rest voltage using a Princeton Applied Research Model273APotentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). The measurement was brought into effect with the cell immersed in the constant-temperature water, and the proton conductivity was calculated by the following formula:

$$\sigma = \frac{L}{RA} \quad (4)$$

where σ is the proton conductivity, L is the distance between the electrodes used to measure the potential ($L = 1$ cm), R is membrane resistance and A is cross-sectional area of membrane.

The methanol permeability was measured by using a diffusion cell described in the literature [34,35]. The concentration of methanol was determined by SHIMADZU GC-8A chromatograph. The methanol permeability was calculated with the following formula:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (5)$$

where A (cm^2) and L (cm) are the effective area and the thickness of the membrane, respectively. V_B (ml) is the volume of diffusion reservoir. C_A and C_B (mol L^{-1}) are the methanol concentration in feed and in diffusion reservoir, respectively. DK is the methanol permeability ($\text{cm}^2 \text{s}^{-1}$).

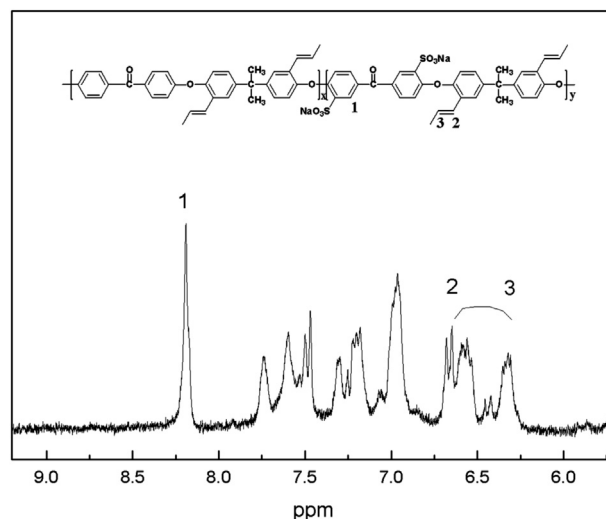


Fig. 1. ^1H NMR of SDPEEK in Na^+ form.

3. Results and discussion

3.1. Structure characterization

The structure of the SDPEEK (in Na^+ form) was confirmed by ^1H NMR spectroscopy. As shown in Fig. 1, the signals from 6.3 to 6.7 ppm were assigned to the propenyl groups while the signal at 8.2 ppm was assigned to electron-withdrawing $-\text{SO}_3\text{Na}$ groups which were consistent with our previous work [36]. The ^1H NMR spectroscopy showed that the SDPEEK was successfully synthesized.

3.2. Thermal stability

The thermal properties of SDPEEK-n(S/E/N) in acid form were assessed using thermogravimetric analysis (TGA). As shown in Fig. 2 and Table 2, all of the membranes have excellent thermal stabilities, and the 5% weight loss temperatures were all above 240 °C. There were two degradation steps observed from the curves. The first weight loss (220 °C–400 °C) was assigned to the decomposition of the sulfonic acid groups, and the second

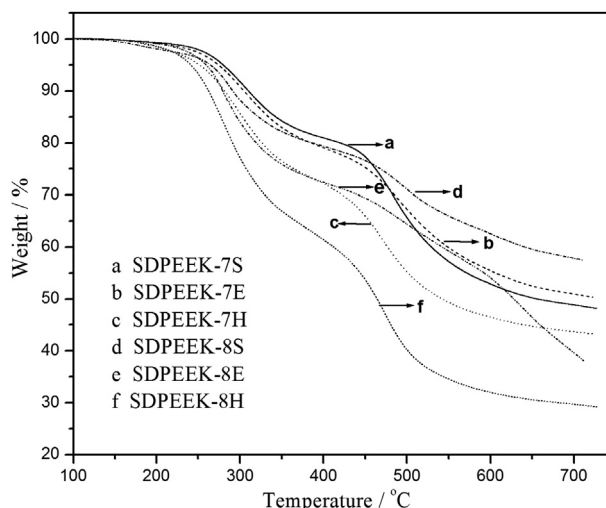


Fig. 2. The TGA curves of the cross-linked membranes in H^+ form under N_2 .

Table 2IEC, Td_{5%}, gel fraction and mechanical properties of the cross-linked membranes.

Membranes	IEC (mequiv g ⁻¹)	Gel fraction ^a (%)	Young's modulus (GPa)	Tensile strength (MPa)	Elongations at break (%)	Td _{5%} °C
SDPEEK-7S	1.79	42.11	0.93	39	5.7	280
SDPEEK-7E	1.56	90.86	1.27	59	9.1	275
SDPEEK-7H	1.30	100.00	1.00	41	11.2	252
SDPEEK-8S	1.83	38.67	0.74	35	7.1	265
SDPEEK-8E	1.66	87.13	0.93	39	9.5	260
SDPEEK-8H	1.53	100.00	0.76	35	14.0	242
Nafion 117 [37]	0.90	—	0.18	38	301.5	—

W₁: the initial weight of membranes W₂: the weight of the cross-linked membranes after marinating in NMP for 24 h at 60 °C, then washed with the deionized water for several times and dried at 100 °C for 24 h.

^a Gel fraction (%) = W₂/W₁ × 100.

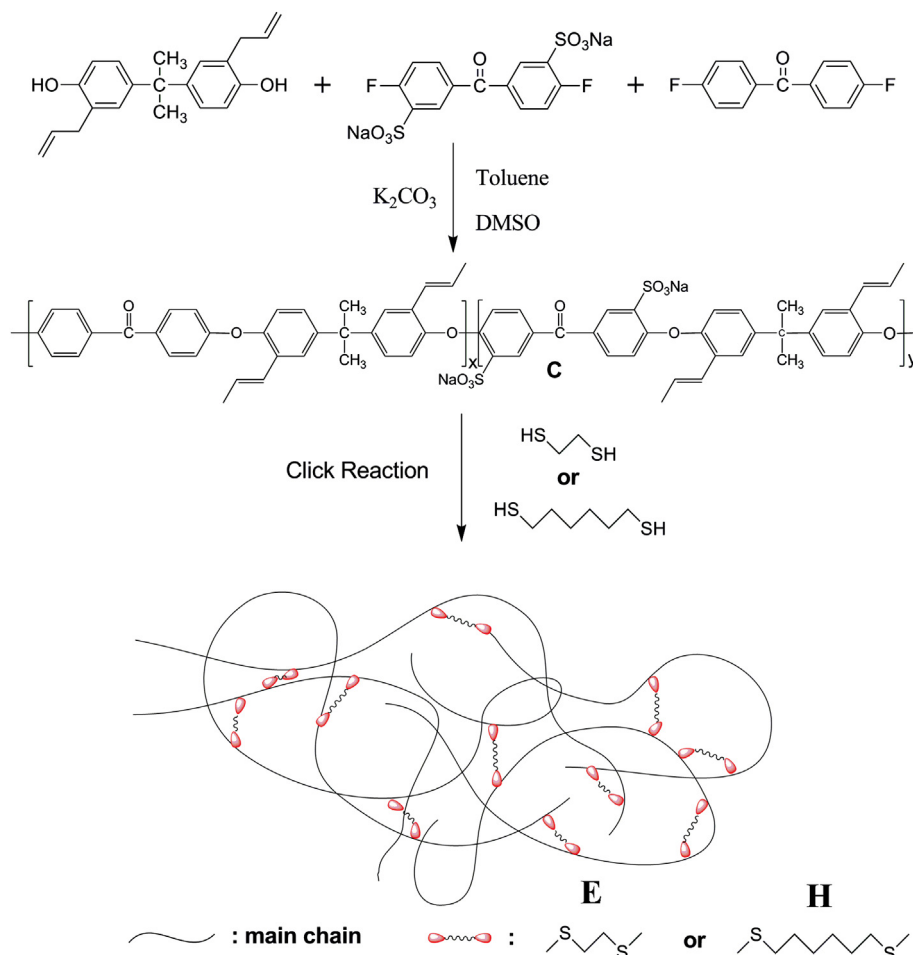
degradation step after 450 °C was attributed to the decomposition of the main chain of the SDPEEK. As seen in Table 2, we could easily find that the 5% weight loss temperatures of SDPEEK-7 membranes were higher than membranes of SDPEEK-8. This phenomenon further verified the higher sulfonated degree of SDPEEK-8. Meanwhile, membranes of SDPEEK-nS showed higher decomposition temperatures than SDPEEK-nE and SDPEEK-nH. It might be caused by the broken of thioether bond (–S–).

3.3. IEC, gel fraction and mechanical properties of the membranes

The IEC value, which indicates the density of sulfonic groups in membranes, influences the water uptake and proton conductivity

directly. As shown in Table 2, SDPEEK-8 membranes possessed higher IEC than SDPEEK-7 membranes which were caused by the different degrees of sulfonation. The cross-linking reagent showed great effect on the IEC values of the membranes. For instance, under the same degree of sulfonation, the variation of IEC presented a rule which was SDPEEK-nS > SDPEEK-nE > SDPEEK-nH, due to the activity of the sulfonic groups restrained by the three-dimensional networks. Another factor caused the reduction of IEC was that thiol was an invalid component for proton conductivity, which made the concentration of sulfonate acid group decrease.

The gel fraction was obtained from the ratio of the weight of the cross-linked membranes after being immersed in NMP for 24 h at 60 °C and the initial weight, which could be considered as an



Scheme 1. Synthesis water soluble sulfonated poly(ether ether ketone) containing dipropenyl groups (SDPEEK-7/8).

Table 3

Water uptake, methanol uptake, water swelling ratio, methanol swelling ratio, proton conductivity, methanol permeability and relative selectivity of the cross-linked membranes.

Membranes	Water uptake %		Methanol uptake %	Water swelling ratio %		Methanol swelling ratio %	Proton conductivity ^a S cm ⁻¹		Proton conductivity S cm ⁻¹ (RH 75%)	Methanol permeability 10 ⁻⁷ cm ² s ⁻¹	Relative selectivity
	20 °C	80 °C		20 °C	80 °C		20 °C	80 °C			
SDPEEK-7S	63.98	351.22	238.61	6.49	40.25	41.67	0.068	0.111	0.029	3.76	5.69
SDPEEK-7E	45.50	181.57	72.86	5.56	32.91	16.00	0.074	0.184	0.017	3.30	6.99
SDPEEK-7H	9.20	20.4	19.10	4.62	9.23	6.12	0.081	0.168	0.014	0.48	52.31
SDPEEK-8S	59.81	480.55	606.02	20.34	54.24	53.33	0.088	0.088	0.033	5.82	4.74
SDPEEK-8E	55.77	222.55	321.82	3.03	23.81	23.15	0.085	0.202	0.027	4.13	6.43
SDPEEK-8H	18.57	30.63	36.04	0.80	12.3	12.74	0.099	0.189	0.019	0.63	49.26
Nafion117 [39]	18.3	27.9	—	10.6	17.2	—	0.076	0.146	—	23.80	1.00

^a The measurement was made with all the membranes immersed in water.

indirect measurement of the cross-linking density. Table 2 shows the gel fractions of the membranes. The membranes which used thiol as the cross-linker performed a much higher gel fraction than the cross-linked membranes with BPO. It indicated that “Click” reaction initiated by the thiol was more complete than the self cross-linking reaction. Therefore, we could demonstrate that in the given condition, the activity of “Click” reaction between the propenyl groups and ethanethiol is much higher than propenyl groups reaction, so that the membranes of SDPEEK-nE and SDPEEK-nH showed higher gel fractions. Furthermore, compared with SDPEEK-nH which has 100% of gel fraction, SDPEEK-nE has a slight lack of gel fraction. It could be inferred that the short molecular chain of 1,2-Ethanedithiol could lead to a more complete reaction with the propenyl groups at the meantime.

PEMs must have superior mechanical strength to be used in fuel cells. Table 2 lists the mechanical properties of the membranes. The Young's modulus of SDPEEK-nE and SDPEEK-nH were in the range 0.76–1.27 GPa surpassed the SDPEEK-nS membranes. All the membranes showed elongations at break between 5.7% and 14.0%, and tensile strengths of 35–59 MPa. These data indicated that the cross-linked network structure restricted the motion of the polymer chains and resulted in tougher membranes which were strong enough to be used as PEMs (Scheme 1).

3.4. Water uptake, water swelling ratio, methanol uptake and methanol swelling ratio

Water uptake performs an important role on the PEMs. PEMs with sulfonic acid groups are typically poor proton conductors

without the presence of water [38]. However, excess water uptake often leads to large dimensional changes in the membranes which bring severe loss in mechanical properties and high methanol permeability. Therefore, it is of great significance to control lower water uptake and swelling ratio for PEMs. Table 3 and Fig. 3 show the water uptakes of the cross-linking membranes at different temperatures. As shown in Fig. 3, cross-linked membranes performed a promoted ability of water uptake as increasing temperature. Water uptake of SDPEEK-nS was the highest. At 80 °C, the membranes of SDPEEK-8S and SDPEEK-7S showed water uptakes of 480.55% and 351.22%, respectively. These results suggested that although the self-crosslinking method improved the stability of the membranes, the relatively low degrees of crosslinking were not sufficient to restrict the water uptake of sulfonic acid groups as SDPEEK-nS membranes possessed higher degree of sulfonation. For instance, SDPEEK-8H and SDPEEK-7H had the same degree of sulfonation as SDPEEK-nS, but the cross-linked membranes reacted by “Click” displayed greatly reduced water uptake of 30.63% and 20.4%, respectively. This phenomenon illustrated that adequate cross-linking was effective to limit the water uptake of membranes. Meanwhile, methanol uptakes of all the cross-linked membranes showed similar rule with water uptakes. According to the different degree of sulfonation, the membranes displayed different methanol uptakes. Table 3 shows the methanol uptakes of the cross-linking membranes at 20 °C. SDPEEK-nS possessed the highest methanol uptakes the same as the role of water uptakes at 20 °C. SDPEEK-8S and SDPEEK-7S showed methanol uptakes of 606.02% and 238.61%, respectively. It inferred that the relatively low degree of cross-linking was not enough to restrict the methanol uptakes of the membranes which possessed the higher degree of sulfonation. Compared with the self-crosslinked membranes, the thiol-crosslinked membranes exhibited less methanol uptakes was attributed to the higher degree of cross-linking. For instance, SDPEEK-7E and SDPEEK-8E showed methanol uptakes of 72.86% and 321.82%. In addition, SDPEEK-7H and SDPEEK-8H showed methanol uptakes of 19.10% and 36.04%, respectively.

Fig. 4 presents the swelling ratios of the cross-linked membranes thickness at different temperatures. It was obvious that the swelling ratios of all the membranes were less than 9% at 20 °C in thickness except SDPEEK-8S. When the temperature rose to 80 °C, SDPEEK-7S and SDPEEK-8S exhibited better swelling ratios in thickness which reached to 40.25% and 54.24% respectively. For comparison, SDPEEK-7H (100% gel fraction) displayed a low swelling ratio (only 9.23% at 80 °C). It also proved that adequate cross-linking degree can significantly improved the dimensional stabilities of PEMs. In Table 3, it was obvious that the swelling ratios of all the membranes in methanol were higher than water at 20 °C. The swelling ratios in methanol of SDPEEK-7S and SDPEEK-8S reached to 41.67% and 51.33%, respectively. It could be

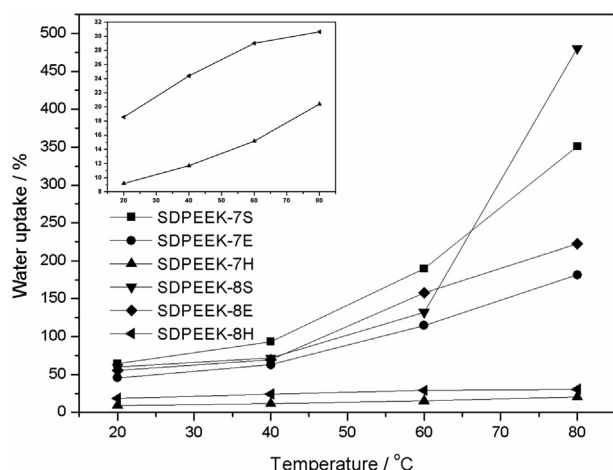


Fig. 3. Water uptakes of cross-linked membranes.

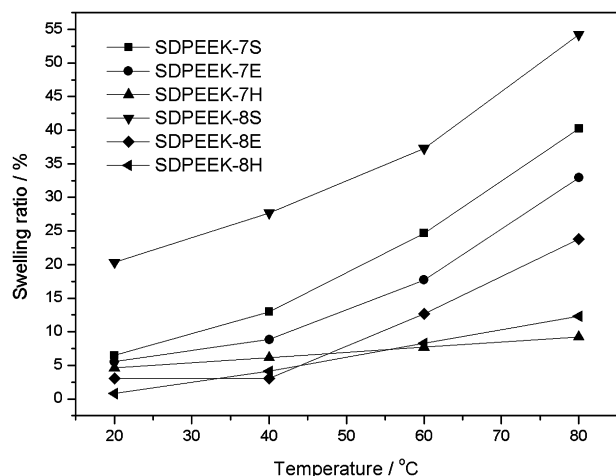


Fig. 4. Swelling ratios of the cross-linked membranes in thickness.

attributed to the less degree of cross-linking. For comparison, thiol-crosslinked membranes possessed higher gel fraction than 87% and displayed a series of low swelling ratios in methanol. Especially, the methanol swelling ratio of SDPEEK-7H was only 6.12% at 20 °C. Therefore, sufficient cross-linking could not only reduce the water swelling but also could decline the methanol swelling ratio.

3.5. Proton conductivity, methanol permeability and selectivity

The performance of a fuel cell is largely determined by the proton conductivities of the PEMs. Table 3 illustrates that all the membranes exhibited high proton conductivities which were measured both in the constant-temperature water and 75% RH. At 80 °C, the membranes showed much higher proton conductivity than Nafion 117 (0.146 S cm^{-1}) except SDPEEK-7S and SDPEEK-8S. Fig. 4 indicates that low gel fraction, which SDPEEK-7S and SDPEEK-8S membranes possessed, had not been sufficient to restrict the water uptake of sulfonic acid groups. Sufficient water uptake could improve proton conductivity when the IEC of the membranes were similar. However, excess water uptake could lead to the dilution of the sulfonic acid groups in the membranes [40]. Thus, the proton conductivity of the SDPEEK-nS was lower than those of SDPEEK-nE/SDPEEK-nH. For instance, SDPEEK-8E with proper water uptake not only showed the highest proton conductivity 0.202 S cm^{-1} among the cross-linked membranes, but also

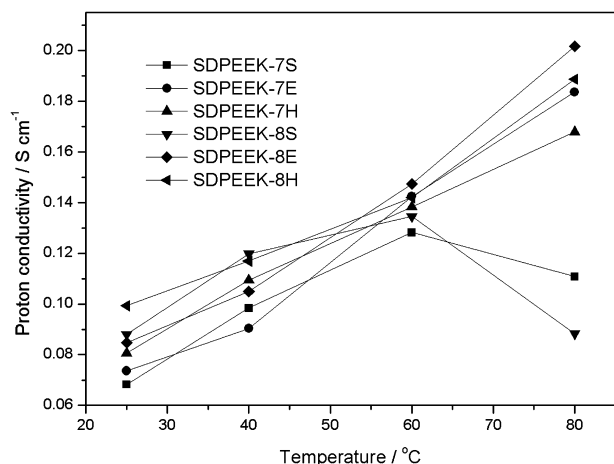


Fig. 5. Proton conductivity of the cross-linked membranes.

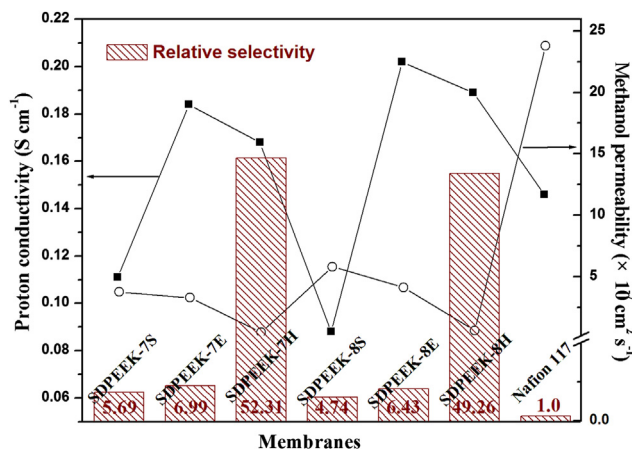


Fig. 6. The relative selectivity of the cross-linked membranes.

preserved the density of the sulfonic acid groups in the membranes. In a relative humidity of 75%, all the membranes exhibited much lower proton conductivities. However, the conductivities of all the self-crosslinked membranes declined less severe than other membranes. This phenomenon could be attributed to the relatively similar water uptakes of the different membranes under the relative humidity of 75%. We have already illustrated that immersed in water, the excess water uptake might dilute the concentration of the sulfonic group and further led to the decline of the conductivity. However, under lower RH, the self-crosslinked membranes possessed the proper water uptake which was not high enough to dilute the concentration of the sulfonic groups. In this situation, the self-crosslinked membranes showed better conductive abilities than other membranes. Given the higher IEC values of the self-crosslinked membrane, it was a normal result. Especially, other membranes possessed higher gel fractions which reflected higher crosslinking degrees, which might restrict the move of the sulfonic groups.

Table 3 lists the methanol permeability and selective parameter of the membranes. All the membranes exhibited methanol permeability in a range of $0.46 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ to $5.82 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which were all much lower than that of Nafion 117 ($2.38 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). As previously reported, water and methanol permeation take place through the same pathway in the membrane, namely the hydrophilic cluster channels [41]. Therefore, it also interpreted that adequate cross-linking played a decisive role of reducing methanol permeability. As shown in Fig. 5, the membrane which possessed a higher gel fraction displayed lower methanol permeability than other membranes with the same degree of sulfonation. It implied that the cross-linking restricted the hydrophilic domains and limited the swelling of the membranes, which resulted in a more tight membrane structure that effectively resisted methanol penetration. The selectivity (the ratio of proton conductivity to methanol permeability) is a common metric for evaluating the membrane performance. Table 3 lists the relative selectivity of the cross-linked membranes. The relative selectivity of all the cross-linked membranes was higher than that of Nafion 117 as shown in Fig. 6, especially SDPEEK-7H membrane, which showed 52 times higher selectivity than that of Nafion 117. The results suggested that the cross-linked membranes could be potentially used for DMFC applications.

4. Conclusions

A series of cross-linked membranes based on water soluble polymer (SDPEEK-7/SDPEEK-8) have been successfully prepared

with self cross-linked and “Click” reaction. Due to different content of cross-linker, the cross-linked membranes displayed excellent properties of thermal stability, water uptakes and swelling ratios. The SDPEEK-8E membrane exhibited the highest proton conductivity 0.202 S cm^{-1} at 80°C while SDPEEK-7H showed the lowest swelling ratios. Furthermore, the selectivity of all the cross-linked membranes was higher than that of Nafion 117. All the results indicated that the series cross-linked membranes were promising candidates in potential application as PEM materials in DMFCs.

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